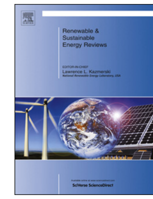
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# A review of solar thermal refrigeration and cooling methods

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ABSTRACT

Energy is the lifeblood of the modern world. Because of the negative environmental impacts and limited sources of fossil fuels, researchers are increasingly focusing on renewable energy sources, particularly solar energy due to its cleanliness and natural availability. Along with photovoltaic systems, solar thermal energy has been used over the last few decades to meet the refrigeration needs for both domestic and industrial purposes. This study presents a review of different solar thermal refrigeration systems, with a specific focus on solar absorption refrigeration systems and solar adsorption refrigeration systems within various working fluids. The different working pairs are illustrated by considering their coefficients of performance, specific cooling power, cooling capacity and minimum and maximum working temperatures. By considering cooling efficiency and other problems, such as swelling and agglomeration, the study also explores solar thermal hybrid cooling systems with heterogeneous composite pairs.



**Contents**



## 1. Introduction

Energy is the soul of the modern world. The economic growth and technological advancement of every country depends on it [1],

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and the amount of available energy reflects that country's quality of life. Three vital factors—economy, population and per capita energy consumption—have caused the increase in demand for energy during the last few decades, making reliable energy one of the massive challenges for the 21st century [2]. From the very beginning of human evolution, man has sought to harness different types of energy. For example, man created fire through the friction of two stones to burn something to provide light and heat. Throughout history, man has discovered other energy resources such as gas, oil, and coal. These fossil fuels are used in the modern world for transportation, communication, industrial, educational and domestic purposes for heating, cooling, cooking, lighting and industrial as well as domestic appliances. However, concern grows daily over the negative impacts fossil fuels have on the environment, whether from their limited sources or their responsibility for global warming through depletion of the ozone layer. $CO_2$ (carbon dioxide) is produced when fossil fuels are burned, causing an increase to the earth's temperature and a green-house gas effect on the atmosphere's ozone layer [3].

The Vienna Convention for the Protection of the Ozone Layer (1985), the Kyoto Protocol on Global Warming (1998) and the five amendments of the Montreal Protocol (1987) all discussed the reduction of CFCs (chlorofluorocarbons) to protect the ozonosphere, but the situation continues to decline. According to the latest NASA investigation, the holes in the ozonosphere over the two poles currently occupy approximately 28,300,000 $km^2$, up from approximately 24,000,000 $km^2$ in 1994 [4]. As a consequence, the EC (European Commission) Regulation 2037/2000, implemented on 1 October 2000, works to control and schedule all the ozone depleting materials; all HCFCs (hydro-chlorofluorocarbons) will be prohibited by 2015 [5,6]. The issue remains of seeking an alternative to fossil fuels before they deplete and/or destroy the earth [3]; renewable energy is the best alternative.

### 1.1. Renewable energy

The term "renewable energy" refers to energy that is produced from a natural resource having the characteristics of inexhaustibility over time and natural renewability. Renewable energy sources include hydropower, wind, biomass, geothermal, tidal, wave and solar energy sources [2]. There have been numerous efforts undertaken by developed countries to implement different renewable energy technologies. The use of wind energy has dramatically increased over the last few years; for example, the Netherlands and Germany are using wind turbines in the north and west for producing electricity [7], and some Asian countries, such as India and Malaysia, have constructed wind turbine power plants to generate electricity. In Mangil City (in northern Iran), there are numerous wind turbines, and in northwestern Iran, mineral materials are used for the production of geothermal energy [8]. In Iceland, seventy percent (70%) of their factories utilize geothermal energy for industrial purposes [9]. This type of energy is cost-effective and pollution-free compared to fossil fuels [3]. Considerable amounts of energy are produced from renewable sources all over the world. Fig. 1 shows the comparative energy generation in Crete in 2005.

Among all these environmentally friendly and naturally available sources, solar energy stands out on the list of renewable energy sources [2].

### 1.2. Solar energy

Because of the threat of a global energy shortage, scientists have increasingly paid more attention to solar energy in recent years [11]. There are plenty of technologies currently available to capture and hold the sun's power for uses such as water heating, cooking, space heating, power generation, food drying and refrigeration [1].

Solar energy is the result of electromagnetic radiation released from the Sun by the thermonuclear reactions occurring inside its core. The properties of this light radiation are visible, infrared and ultraviolet. All of the energy resources on earth originate from the sun (directly or indirectly), except for nuclear, tidal and geothermal energy. The sun actually transmits a vast amount of solar energy to the surface of the earth [12]. The term "solar constant, $S_c$" signifies the radiation influx of solar energy. Choudhury et al. [13] calculated a mean solar constant value equal to 1368 $W/m^2$. Therefore, considering a global plane area of $1.275 \times 10^{14}$ $m^2$ and the mean radius of the earth being approximately 6371 km, the total radiation transmitted to the earth is $1.74 \times 10^{17}$ W [8].

Most countries are now accepting that solar energy has enormous potential because of its cleanliness, low price and natural availability. For example, it is being used commercially in solar power plants. Sweden has been operating a solar power plant since 2001. Additionally, Turanjanin et al. [14] described the solar-heated water plant situated in the rural areas of Iran. In their studies, they also observed the irradiances of solar radiation in Belgrade for an entire year and concluded that the maximum radiation occurs from May to September.

In recent years, many countries have been facing difficulties with the issue of refrigeration systems. Specifically, the demand of air conditioning for both commercial and residential purposes during the hot season is ever-increasing [12]. There is a lack of electrical energy and storage in developing countries to accommodate high energy consumptive systems such as refrigeration and cooling. Therefore, solar cooling technologies have become a worldwide focal point; this energy crisis has opened the door for solar energy to handle not only peak electricity demands but also cooling issues.

### 1.3. Solar refrigeration

Solar refrigeration engages a system where solar power is used for cooling purposes [15]. Solar energy can provide cheap and clean energy for cooling and refrigeration applications all over the world. For example, the implementation of a solar-driven cooling

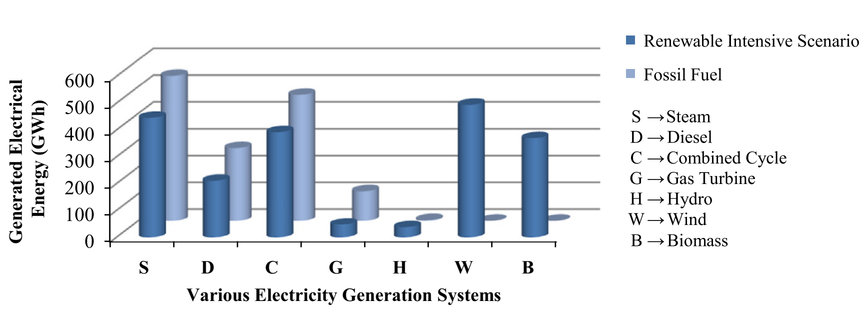



**Fig. 1.** Electricity generation in Crete in 2005 [10].

system can save the Mediterranean countries approximately 50% of their energy costs [8]. Solar energy also has vast applications for the agricultural sector. Solar pumps can be used for irrigation. Maintaining and storing crops is very difficult where electricity is unavailable; solar refrigeration can definitely play an important role [16]. Moreover, some sub-Saharan countries that have very good solar potential can use solar refrigeration for storing medicines and vaccines at lower temperatures, and these systems can be made portable if needed, as their energy source is the sun [17].

Solar refrigeration has become more attractive for cooling purposes today because of the use of desiccant gases, such as LiCl (lithium chloride) and LiBr (lithium bromide), or water instead of harmful Freon gas [18]. Cooling can be achieved through two basic methods. The first is a PV(Photovoltaic)-based solar energy system, where solar energy is converted into electrical energy and used for refrigeration much like conventional methods [19]. The second one utilizes a solar thermal refrigeration system, where a solar collector directly heats the refrigerant through collector tubes instead of using solar electric power [12]. This review will focus on the second method.

#### 1.3.1. Solar photovoltaic cooling systems

A PV cell is basically a solid-state semiconductor device (much like a computer chip) that converts light energy into electrical energy. Small PV cells are typically used in wrist watches and calculators, whereas the larger ones are used for supplying power for industrial and domestic electrical appliances, such as lights, fans, heaters, motors, refrigerators, etc. To accommodate the huge demand for electricity, PV-based electricity generation has been rapidly increasing around the world alongside conventional power plants over the past two decades [20]. Fig. 2 shows a comparative representation of the development of solar PV systems in the USA, Japan, European countries and the rest of the world.

While the output of a PV cell is typically direct current (DC) electricity, most domestic and industrial electrical appliances use alternating current (AC). Therefore, a complete PV cooling system typically consists of four basic components: photovoltaic modules, a battery, an inverter circuit and a vapor compression AC unit [21].

- **The PV modules:** The PV cells produce electricity by converting light energy (from the sun) into direct current (DC) electrical energy.
- **The battery:** The battery is used for storing DC voltages at a charging mode when sunlight is available and supplying DC electrical energy in a discharging mode in the absence of daylight. It can also directly handle DC uses for both industrial and home appliances. A battery charge regulator can be used to protect the battery form overcharging.
- **The inverter:** The inverter is an electrical circuit that converts the DC electrical power into AC and then delivers the electrical energy to the AC loads.
- **The AC unit:** The vapor compression AC unit is actually a conventional cooling or refrigeration system that is run by the power received from the inverter.

The PV system can perform as a standalone system, a hybrid system (working with an oil/hydro/gas power plant) or as a grid or utility intertied systems. Fig. 3 shows a standalone PV system.

Though the efficiency of PV modules can be increased by using inverters, their COP and efficiency are still not desirable. Attention must then be given to Solar Thermal Refrigeration systems for cooling purposes.

#### 1.3.2. Solar thermal cooling systems

Thermal cooling technology is preferred to PV-based cooling systems because it can utilize more incident sunlight than a PV system. Fig. 4 shows a clear partition of incident solar power when it falls on a formal photovoltaic collector. It shows that most of the total solar energy converts into heat, and a very small portion produces electricity in a PV system, with 65% of the incident rays (infrared rays, red and orange) converted into heat energy and only 35% useful for generating electricity in a silicon-based PV system [21]. Therefore, thermal solar cooling is becoming more popular because a thermal solar collector directly converts light into heat. For example, Otanicar et al. [21] described a thermal system that is capable of absorbing more than 95% of incident solar radiation, depending on the medium.

A solar thermal refrigeration system consists of four major components: a solar collector array, a tank for thermal storage, a thermal AC unit and a heat exchanger [21]. The thermal collector receives the light energy from the sun and increases in temperature; as a result, the refrigerants inside the collector evacuated tubes become hot through a heat convection process. The thermal storage tank is used for storing the hot refrigerants from the collector tubes. The thermal AC unit is run by the hot refrigerant coming from the thermal storage tank, and the refrigerant circulates through the entire system. The heat exchanger is responsible for transferring heat between the hot and cold spaces [15]. Fig. 5 shows a schematic diagram of a solar thermal cooling system.

Sorption technology is utilized in thermal refrigeration techniques; the cooling effect is obtained from the chemical or physical changes between the sorbent and the refrigerant. Sorption technology can be classified either as open sorption systems or closed sorption systems. In closed sorption technology, there are two basic methods: absorption refrigeration and adsorption refrigeration [23]. This study focuses on these two closed sorption cooling systems with a brief comparative study.

## 2. Absorption refrigeration

Absorption is the process in which a substance assimilates from one state into a different state. These two states create a strong

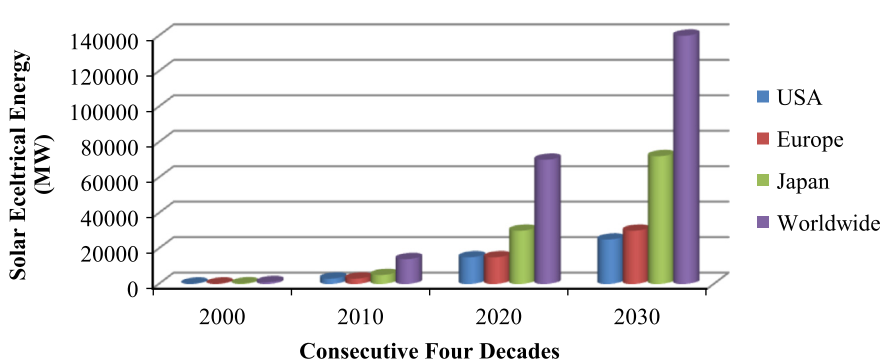



**Fig. 2.** Global PV-based solar electrical energy production over four decades [20].

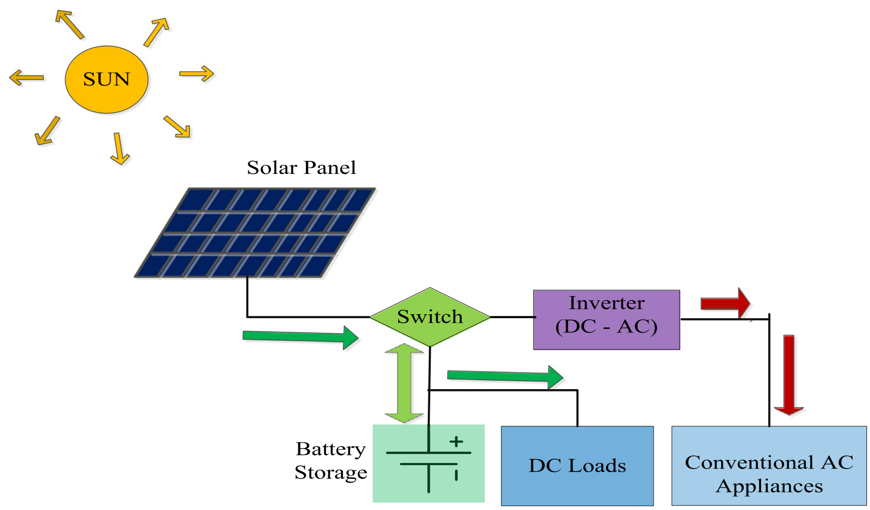



**Fig. 3.** Schematic diagram of a standalone PV system [21].

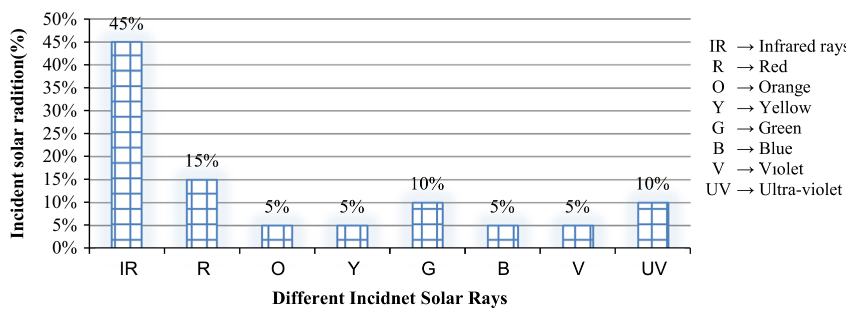



**Fig. 4.** Distribution of incident solar rays used in a PV system [21].

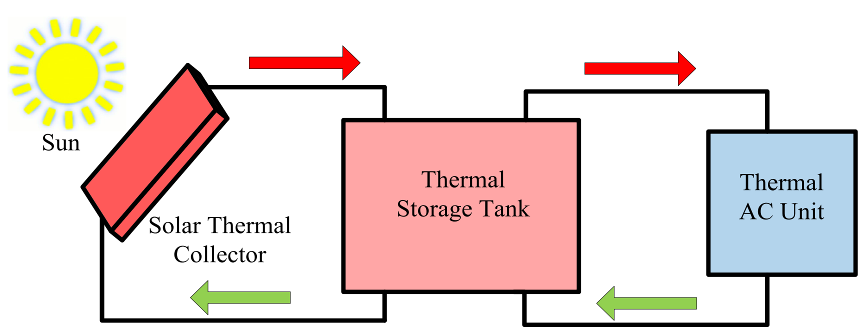



**Fig. 5.** Schematic diagram of potential solar thermal cooling system [22].

attraction to make a strong solution or mixture. The increase of heat in a solution can reverse the process [24]. The first evolution of an absorption system began in the 1700s. It was observed that in the presence of $H_2SO_4$ (sulfuric acid), ice can be made by evaporating pure $H_2O$ (water) within an evacuated container. In 1810, it was found that ice could be produced from water in a couple of vessels connected together in the presence of sulfuric acid. As the $H_2SO_4$ absorbed water vapor (to reduce heat), ice formed on the surface of water. However, difficulties emerged with leakage and the corrosion of air into the void vessel. In 1859, a French engineer named Ferdinand Carre designed a machine that used a working fluid pair of water and ammonia. This machine was used for making ice as well as storing food, and he filed for a US patent in 1860. In 1950, a new system was introduced with a water/lithium–bromide pairing as working fluids for commercial purposes [25]. The primary advantage of an absorption system is that it has a larger COP (coefficient of performance) than other thermally operated technologies.

### *2.1. Absorption cooling working pairs*

The pair of working fluids plays a crucial role in absorption cooling system. The COP of an absorption system depends on both the physical and chemical properties of the system [26]. The basic requirement of a pair of working fluids is that they have a bound of miscibility between them in the range of certain operating temperatures in a liquid phase. Along with this requirement, the following important criteria should be considered carefully [27]:

- The working pair should be pollution-free, non-corrosive and cost-effective.
- The boiling points between the mixture and pure refrigerant should have a large differential under a constant pressure.
- To maintain the low circulation rate of the refrigerant, it should have a high concentration and latent heat within the absorbent.
- The thermal conductivity, viscosity and diffusion coefficient should be favorable.

- The volatility of the refrigerant should allow it to be separated from the absorbent without a filter.
- The solution should be chemically stable, non-toxic and non-explosive.

There are many working pairs used all over the world. Marcris [28] categorized over 200 absorbents with more than 40 refrigerant compounds.

Among all the working fluids for absorption systems, the most widely used pair, for both heating and cooling purposes, is water–ammonia ($H_2O/NH_3$) [29]. In this case, $NH_3$ works as the refrigerant and $H_2O$ as the absorbent, and both of them exhibit high stability under a wide range of working pressures and temperatures. Ammonia has a high latent heat of vaporization, and because its freezing point is approximately −77 °C, it can be utilized at very low temperatures [27]. Because this pair is volatile, a rectifier is required to separate the water from the ammonia; otherwise, system performance will decrease. Although this pair has a highly corrosive and toxic reaction with copper, its use is pollution-free and cost-effective compared to other pairs. The thermodynamic characteristics of $H_2O/NH_3$ have been described in various studies and experiments [30,31].

The second most important working pair in absorption technology is lithium–bromide and water ($LiBr/H_2O$). The use of this pair dates from 1930 [32]. It overcomes the problem of using a filter as the pair is not volatile, and it has a very high latent heat of vaporization. However, because water is used as the refrigerant in this pair, there are problems with low temperature operation at temperatures below 0°C. Moreover, the system requires vacuum conditions and at high concentrations, the pair tends to be crystalline. There are also issues of corrosion with some metals. A brief thermodynamic analysis of this pair is available in previous investigations [33,34]. Wen and Lin [35] have suggested using additives in the pair to reduce corrosion. Other suggestions have come from studies conducted to further develop the performance of heat and mass transfer [36,37].

Even though $H_2O/NH_3$ and $LiBr/H_2O$ pairs have been used all over the world, researchers are still looking for new pairs. For example, de'Rossi et al. [38] have introduced some new pairs; among them, R21 and R22 has been broadly suggested as new working pairs because they have greater solubility with organic solvents [39].The two important solvents, DMF (dimethyl formamide) and DMETEG (dimethyl ether of tetra-ethylene glycol), have been discussed in previous literature and analyses [40,41].

## 2.2. Solar absorption cooling systems

The absorption refrigeration technology consists of a generator, a pump and an absorber that are collectively capable of compressing the refrigerant vapor. The evaporator draws the vapor refrigerant. The extra thermal energy separates the refrigerant vapor from the solution. The condenser condenses the refrigerant, and then the cooled refrigerant is expanded by the evaporator [42,43].

In solar thermal absorption refrigeration technology, the chiller is used to absorb heat from the tank attached to the solar collector. According to the solution regeneration and thermal operation cycle, the absorption systems can be divided into three categories: single-effect, half-effect and double-effect solar absorption cycles. The single-effect and half-effect chillers require lower temperatures with respect to a double effect-chiller [23]. There are also two other absorption refrigeration systems (DAR (diffusion absorption refrigeration) and hybrid systems) that can achieve better performance [42].

### 2.2.1. The single-effect solar absorption cycle

Recent statistics show that most absorption refrigeration systems are made using single-effect absorption technology with a LiBr/water pair, where a solar flat-plate collector or an evacuated-tubular collector with hot water is used to implement these systems [43]. Raja and Shanmugam [44] outlined an absorption system that used $LiBr–H_2O$ as working pair. Fig. 6 shows a single-effect absorption refrigeration system for a $LiBr–H_2O$ pair.

The cycle starts at the absorber. The absorber receives the vapor-refrigerant from the refrigerator and creates a rich-mixture. The pump forwards this mixture to the generator or the high-pressure zone (disorber). In the generator, the refrigerant is then separated from the absorbent by the heat provided by the solar collector. Using a pressure-relief valve, the weak-solution then returns to the absorber. A SHX (solution heat-exchanger) is in place to recover the internal heat [24]. It is also responsible for preheating the outgoing rich-solution from the absorber, improving the system efficiency and resisting the irreversibility of the cycle. A 60% higher COP can be achieved by using the SHX [45]. The refrigerant then follows the conventional cycle through the condenser, expansion valve and evaporator [24].

A single-effect absorption cooling system is simpler than others when the design depends on the types of working fluids. The system shows better performance with non-volatile absorbents such as LiBr/water. If a volatile working pair such as ammonia/water is used, then an extra rectifier should be used before the condenser to provide pure refrigerant [25]. Rosiek and Batlles [46] investigated a single-effect solar absorption cooling system at the Solar Energy Research Center, Spain. They observed an energy demand for heating of approximately 8124 kWh,

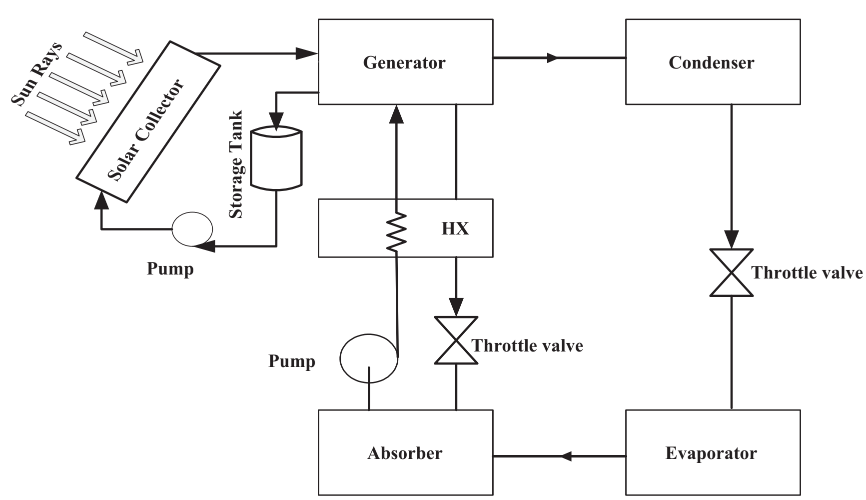



**Fig. 6.** A solar assisted single-effect $LiBr–H_2O$ absorption cycle [44].

whereas the cooling demand was approximately 13,255 kWh throughout the year. The system consisted of 160 $m^2$ of flat-plate collectors and an absorption chiller of 70 kW with a data acquisition system (DAS). They found an average cooling capacity of 40 kW with an average COP of 0.6. Ortiz et al. [47] performed an experiment with a Yazaki single-effect LiBr/$H_2O$ fired-chiller. They used the flat-plate collectors of approximately 124 $m^2$ with vacuum tubular-collectors of 108 $m^2$. The system was capable to run within a temperature of 70 to 95 °C with a capacity of 70 kW. Rodríguez Hidalgo et al. [48] designed an absorption cooling system for domestic cooling purpose in Spain. They used a flat-plate collector of 50 $m^2$ with a single-effect absorption machine of 35 kW. The LiBr–$H_2O$ working fluids showed a COP of 0.33 during the summer season in 2004. They concluded that by providing an input power of 10–15 kW to the generator, 6–10 kW of cooling power could be achieved within an average time period of 6.5 h.

A domestic-prototype solar refrigeration system was installed by Agyenim et al. [49] in Cardiff University, UK. They used a 4.5 kW absorption-chiller with a solar collector (vacuum tubular type) of 12 $m^2$ and a fan-coil of 6 kW. There was a large cold-storage tank of 1000 l where LiBr and water were used as working fluids, showing a COP of 0.58. The system was able to maintain the temperature at approximately 7.4 °C, signifying the potential for cooling domestic buildings. Li and Sumathy [50] observed an absorption system with a partitioned hot-water storage tank. The system consisted of a 38 $m^2$ flat-plate collector, a 4.7 kW absorption-chiller and a LiBr–water working pair. They concluded that the system exhibited 15% more COP (approximately 0.7) than a conventional whole-tank mode system.

An investigation was performed by Syed et al. [51] on a LiBr/water absorption system consisting of 49.9 $m^2$ of flat-plate collectors. The system performed refrigeration within generator temperatures of 65–90 °C, maintaining a capacity of 35 kW. They calculated three different COPs and achieved an average collector efficiency of approximately 50%. Another experiment on a single-effect absorption system with the same pair was performed by Praene et al. [52]. The system was installed at the Institut Universitaire Technologique of Saint Pierre with a capacity of 30 kW; it was able to maintain a temperature of approximately 25 °C inside the classrooms.

### 2.2.2. The half-effect solar absorption cooling system

The primary feature of the half-effect absorption cycle is the running capability at lower temperatures compared to others. The name “half-effect” arises from the COP, which is almost half that of the single-effect cycle [24].

Arivazhagan et al. [53] performed an experiment with a two-stage half-effect absorption system using the working pair of DMAC(absorbent)/R134a (refrigerant). They were able to attain an evaporation temperature of −7 °C with the generator temperature varying from 55 °C to 75 °C. They concluded that within the optimum temperature range (65–70 °C), a COP of approximately 0.36 could be achieved. Gebreslassie et al. [54] performed an exergy analysis for a lithium-bromide/water pair in a multiple-effect absorption system. They conducted a comparative exergy study among single-effect, double-effect and triple-effect absorption for unavoidable destruction. Kim and Machielsen [55] initiated a comparative study on the cost and performance of absorption chillers. They concluded that though chillers required more surface area (40% more) than heat-exchangers and extra collector-areas (10–60% more), they can operate at higher temperatures compared to single-effect chillers.

In another theoretical investigation, Kim and Infante Ferreira [56] worked with a LiBr/water chiller at low temperatures for the purpose of cooling extensively hot and dry regions. They predicted through simulation that the COP would be 0.37 by using chiller water at 7 °C with 90 °C hot water. Sumathy et al. [57] proposed a two-stage LiBr/water chiller for cooling purposes in south China. They found a cooling capacity of 100 kW through the integration of a solar refrigeration system with these chillers. They concluded that the system had a nearly equivalent COP as the conventional cooling system, but at a 50% reduced cost.

Izquierdo et al. [58] designed a solar plant with LiBr/water. The plant contained flat-plate-collectors to feed the generator with a double-stage absorption cycle. They showed that within a condensation temperature of 50 °C, the COP was 0.38 while providing a generation temperature of 80 °C. They also conducted an exergetic analysis of this system and found that the single-effect system had 22% more exergetic efficiency than the double-stage half-effect system.

### 2.2.3. The double-effect solar-assisted absorption cooling systems

Double-effect absorption cooling technology was launched in 1956 for developing the system performance within a heat-source at higher temperatures [59]. Fig. 7 illustrates a double-effect absorption system with a LiBr/water pair.

The cycle begins with generator-I providing heat to generator-II. The condenser rejects the heat and passes the working fluid towards the evaporator; within this step, the required refrigeration occurs. Then, the fluids pass through the heat-exchangers (HX-I and HX-II) from the absorber to generator-I by means of a pump. Through this process, HX-II can pass the fluids to generator-II and then generator-II passes to HX-I. The complete cycle follows three different pressure levels: high, medium and low [25].

Two single-effect systems effectively form a double-effect absorption cooling system; therefore, the COP of a double-effect

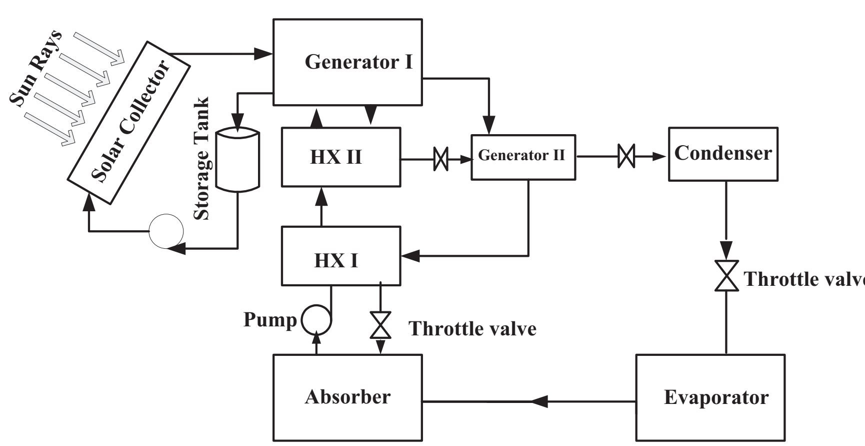



**Fig. 7.** A double-effect LiBr/$H_2O$ absorption system [25].

system is almost twice that of the single-effect absorption system. For example, Srikhirin et al. [25] conducted an analysis showing that the COP of a double-effect system is 0.96, whereas the single-effect system has a COP of only 0.6.

In the past few years, the COP of double-effect absorption systems has reached values of 1.1–1.2 by using gas-fired absorption technology [25]. Qu et al. [60] implemented a double-effect absorption system with LiBr/water chillers of 16 kW. They also used a parabolic solar-collector of 52 $m^2$ with a heat-exchanger and pumps for circulation of the working fluids. There was also a natural gas-burner used to supply heat in the absence of solar energy.

Tierney [61] conducted a comparative study among four different systems with a collector of 230 $m^2$ and concluded that the double-effect chiller with a trough collector had the highest potential savings (86%) among the four systems to handle the demand for a 50 kW load. Liu and Wang [62] designed a double-effect absorption system with a LiBr/Water pair driven by solar or gas. This system can perform feasibly and economically within a generator temperature of 90 °C. The system is capable of adeptly running throughout the year with a capacity of 10 kW.

#### 2.2.4. *The diffusion absorption solar cooling system (Platen–Munters cycle)*

Von Platen and Munters were the pioneers in Sweden who introduced the term "DAR" (diffusion absorption refrigeration) in 1920. They used hydrogen as an inert gas (auxiliary gas) with a water (adsorbent)/ammonia (refrigerant) pair. The DAR concept has been used for the last 8 decades because of the special feature of this system that allows it to operate without any electrical or mechanical energy [63]. Moreover, it can run with a high temperature (>150 °C) source and can therefore be installed anywhere in the world [64].

In fact, the DAR is a self-circulating absorption system in which a bubble-pump is responsible for circulating the fluids. A conventional absorption cooling system pales in comparison, as it is free of any moving parts. It typically has no dynamic component, as the pump works with a single low pressure. During the refrigeration process, the 3rd (auxiliary) fluid assists the main pair to keep the pressure stable for the expansion process [64].

$NH_3/H_2O/H_2$ (ammonia–water–hydrogen) pair is the most widely used working fluid for DAR systems, where hydrogen is the auxiliary fluid with ammonia and water. Though the ammonia/water pair can utilize a heat source of more than 150 °C, lithium bromide works at temperatures below 100 °C. Because water is used as the absorbent in this pair, problems occur when cooling at temperatures lower than 0 °C. Therefore, Koyfman et al. [64] suggested the use of an organic solvent with hydro-chlorofluorocarbon, which is capable of maintaining a temperature below 0 °C. Chen et al. [65] implemented a new-generation absorption cooling system in which they were able to increase the COP by approximately 50%. They used a coaxial heat-exchanger and the bubble-pump that allowed the heat losses to be decreased while increasing the efficiency of the system. Pfaff et al. [66] mathematically designed a DAR system with the lithium bromide/water pair. They inserted a test rig in glass to investigate the performance of a bubble pump with various diameters of pipes and found that when the heat supply was 40 W, the refrigeration capacity was 100 W for a pipe diameter of 10 mm. They concluded that the refrigeration capacity could be increased by using additional bubble pumps in parallel. Zohar et al. [42] conducted a numerical analysis for an ammonia/water pair in a DAR system. Their study showed that approximately 14–20% more COP can be achieved without using the condensate sub-cooling, but the evaporation temperature must be kept above 15 °C.

#### 2.2.5. *The hybrid solar absorption cooling systems*

A hybrid cooling concept arose due to the lack of properties in the above discussion and to integrate different pairs or systems for obtaining better cooling performance [67]. Hybrid solar adsorption cooling technology refers to the integration of three individual cooling technologies: radiant cooling, desiccant cooling and absorption cooling [18]. Fong et al. [68] designed a high-tech office building that was cooled with a hybrid solar cooling system. They divided the entire system into four basic functions: absorption refrigeration, desiccant dehumidification, radiant cooling and collecting solar energy. The first function utilizes an absorption chiller as the core apparatus. A water pump powers the chiller by providing hot water, while a desiccant wheel is the primary component for the desiccant dehumidification function. The third function utilizes active and passive beams and passive chilled-beams specially designed for cooling, and the final function utilizes a flat-plate collector capable of harvesting solar energy without freezing in winter. Table 1 summarizes the above-mentioned absorption cooling systems.

## 3. Adsorption cooling technologies

Faraday first introduced vapor adsorption technology in 1848, using a solid adsorbent. Adsorption cycles were first used in refrigeration and heat pumps in the early 1990s. The disadvantages of liquid–vapor systems were overcome by using solid–vapor cycles; this technology was first marketed in the 1920s [16]. The Nishiyodo Kuchouki Company Ltd. was the pioneer in bringing adsorption refrigeration technology to the US market in 1986 [13].

Adsorption refrigeration technology has been used for many specific applications, such as purification, separation and thermal refrigeration technologies [69]. The adsorption process differs from the absorption process in that absorption is a volumetric phenomenon, whereas adsorption is a surface phenomenon. The primary component of an adsorption system is a solid porous surface with a large surface area and a large adsorptive capacity. Initially, this surface remains unsaturated. When a vapor molecule contacts the surface, an interaction occurs between the surface and the molecules and the molecules are adsorbed on to the surface [2]. An adsorption cooling system is not only advantageous for its zero ODP (ozone depleting potential) but also for other positive features [4,70]:

- Adsorption technology can accommodate high temperature heat sources (over 500V) without corrosion, whereas corrosion occurs above 200 °C in absorption technology.
- Adsorption technology is better equipped to handle vibration issues in a cooling system than absorption technology. Because of the liquid absorbent present in an absorption system, vibrations can cause serious problems, such as flows from the absorber to condenser or from the generator to evaporator, potentially polluting the refrigerant. Adsorption is immune to this condition, and can thus be used in locomotives and fishing boats.
- An adsorption system is simpler to design than an absorption system. For example, to design an absorption system with a $H_2O/NH_3$ working pair, extra equipment (dephlegmate) is required because the boiling points of water and ammonia are very close.

### 3.1. *Working principle of the solar adsorption cooling system*

Adsorption is a process in which molecules of a fluid are attached to a surface. The surface is composed of a solid material.

**Table 1**
The characteristics of the working fluids found from various absorption cooling technologies.

| Absorption cooling systems | Working-pairs | Features/results |
|---|---|---|
| Single-effect cooling | LiBr–$H_2O$, $NH_3$–$H_2O$ | • Approximately 60% more COP can be achieved by using a SHX (solution heat-exchanger) [45]<br>• A rectifier is needed to purify the refrigerant if the pair is volatile [24]<br>• A system capacity of 70 kW can be achieved by using a vacuum tubular-collector (108 $m^2$) with flat-plate collectors (124 $m^2$) [47]<br>• COP can be increased by 15% using a partitioned hot-water tank with a flat-plate collector (38 $m^2$) and chillers (4.7 kW) [50] |
| Half-effect cooling | LiBr–$H_2O$ | • Within the optimum temperature range of 65–70 °C, the COP=0.36 and the evaporation temperature is −7 °C [53]<br>• The pair is capable of providing the same COP as a conventional refrigeration system with reducing the cost by half. [57]<br>• The system has 22% lower exergetic efficiency compared to the single-effect systems [58] |
| Double-effect cooling | LiBr–$H_2O$ | • The system has almost double (0.96) the COP compared to the single-effect system [25]<br>• The double-effect chillers with trough collectors show the maximum potential savings (86%) [61] |
| DAR | $NH_3/H_2O/H_2$, LiBr–$H_2O$/ $H_2$, hydro-chlorofluorocarbon | • More than 150 °C of heat source can be utilized when the working pair is ammonia/water. Organic solvent can be used to run the system below 0 °C [64]<br>• Approximately 50% of COP can be increased by using a coaxial heat-exchanger with a bubble pump [65]<br>• The greater usage of bubble pumps in parallel indicates the better performance of cooling capacity [66] |
| Hybrid cooling | Combination of mentioned pairs | • These types of systems are widely implemented for the cooling of larger places, such as offices, markets or auditoriums [68] |

The molecules do not perform any chemical reaction; they merely discard energy when attached to the surface. The phase change (from fluid to adsorbate) is exothermic, and the process is fully reversible [71].

On an exposed solid surface with a gas, the gas molecules are forcibly thrust upon the surface of that solid. Therefore, some molecules adhere to the surface and become adsorbed while some of them rebound back. At the onset of an adsorption process, the rate of adsorption is greater because the full surface is uncovered [39]. The adsorption rate gradually decreases as the surface becomes more inundated with the adsorbate. Meanwhile, the rate of desorption increases in parallel with the decrease of adsorption, as the desorption occurs from the exposed solid surface. However, equilibrium is achieved when the adsorption rate and desorption rate are equal. This is called adsorption dynamic-equilibrium, as the number of striking molecules on the surface and rebounding molecules from the surface are equal. This equilibrium depends on both the temperature and the pressure of a fixed adsorbate-adsorbent system [1].

### 3.2. Adsorbents and working pairs

In an adsorption refrigeration technique, the working pair plays a vital role for optimal performance of the system. The best performance is achieved if the adsorbent demonstrates the following characteristics [72]:

a. A large adsorption ability.
b. The ability to change capacity with the variation of temperature.
c. A flatter isotherm.
d. Excellent compatibility with the refrigerant.

On the other hand, the refrigerant should also demonstrate certain characteristics for better performance, such as a significant latent heat capacity, exact freezing point and saturation vapor pressure, non-flammability, good thermal stability, anti-toxicity, lack of corruption/adulteration, etc. Unfortunately, there are few working pairs that completely fulfill the requirements discussed above. However, there are some working pairs that come close [4,70,73]:

(i) silica gel/water,
(ii) activated-carbon/methanol,
(iii) activated-carbon/ammonia,
(iv) zeolite/water,
(v) activated carbon granular and fiber adsorbent,
(vi) metal chloride/ammonia,
(vii) composite adsorbent/ammonia,
(viii) metal hydrides and hydrogen,
(ix) metal oxides and oxygen.

According to most sorption techniques, all of these working pairs can be categorized into two specific groups, named “Physisorption” and “Chemisorption”. There are also some hybrid adsorption pairs that have higher COPs than others [70].

#### 3.2.1. Solar physisorption cooling systems

In physisorption technology, the adsorbate molecules form a van der Waals interaction with surface molecules within a vacuum and clean environment instead of forming a chemical bond [4]. Therefore, the adsorption pair remains unchanged in terms of their chemical compositions. There is a similarity between adsorption and the condensation of heat in gas in enthalpy in that both of them have the same order. The presence of a van der Waals interaction requires very low heat (maximum 80 kJ/mole) to break this bond. This technology is completely non-specific and can be used in any adsorbent-adsorbate system. It is also capable of adsorbing continuous layers in a multi-molecular phase [2]. The most common working pairs used in adsorption technology are silica gel-water, activated-carbon-methanol, activated carbon-ammonia, zeolite-water, activated-carbon granular and fiber adsorbent [70].

*3.2.1.1. Silica gel adsorbent.* Silica gel is a static continuous trap of colloid silica attached with tiny grains of hydrated $SiO_4$. In silica gel, adsorption occurs with the presence of a hydroxyl group in its structure. The COP of silica gel adsorption greatly depends on the

polarization of the hydroxyl ions that form hydrogen bonds with oxides [70]. However, overheating can decrease the COP—this technology is suitable only up to 200 °C. The average pore size of silica gel is approximately 650 $m^2$/g. There are two pore diameters —3 nm and 0.7 nm—called type A and type B, respectively, with surface areas of 100–1000 $m^2$/g. Type B pored silica gel is only applicable when the humidity is higher than 50%, while type B is applicable for any condition [16].

Silica gel is usually produced through the partial dehydration of colloidal silicic acid polymer, which is expressed as $(SiO_2)\cdot nH_2O$. Water is used as a refrigerant with the silica-gel adsorbent. For water-vapor silica gel, the adsorption–desorption process is completely physical and illustrated as follows[1]:

$$SiO_2\cdot(n{-}1)H_2O\ \text{(solid)}+H_2O\ \text{(vap)}\leftrightarrow SiO_2\cdot nH_2O\ \text{(solid)}+\Delta H$$

where $\Delta H$ denotes the amount of heat produced during the adsorption process.

There should be no change in shape or size when the saturation of the particles begins, and the particle should be completely dried when full saturation has occurred [74]. This working pair is attractive because it works at a very low temperature. One study [75] showed that the pair can run with a heat source of approximately 50 °C. Moreover, water has the distinct advantage of greater latent heat than methanol or other conventional refrigerants.

However, the drawback of this pair is the low capacity of adsorption as well as low vapor pressure, which can resist mass transfer. Wang et al. [70] reviewed different working pairs used in an adsorption system where the desorption heat is relatively high (2500 kJ/kg) and the desorption temperature was limited to maximum value of 120 °C. This pair thus has limited application for used in refrigeration systems [2].

*3.2.1.2. Zeolite adsorbent.* A zeolite is a alumina-silicate crystal that is formed in alkali systems. Zeolites are represented by the molecular formula $M_{y/n}\ [(AlO_2)_y\cdot(SiO_2)_x]zH_2O$, where $m$ and $y$ indicate the integer numbers such that $m/y \geq 1$, $n$ is the valence number and $z$ is the total water molecules [70]. Natural zeolites can be classified into 40 different types. Among them, the most important types are faujasite, cowlesite, chabazite and sodium chabazite. Zeolites are also produced artificially in the laboratory; over 150 types have been synthesized worldwide. These artificial types are named with a single letter or a group of letters, such as type A, B, X, ZSM, etc. [76]. Although these types of zeolites have a high performance to heat transfer, they are also very expensive. The adsorption capacity depends on the zeolite structure. For example, a truncated octahedral shape is found for types X, Y and A zeolites. A single crystal of these types of zeolites is capable of adsorbing 24 molecules of water. The adsorption occurs in the crystal pores or the center cages [70].

Air conditioning is the primary application of zeolite-water cooling systems because the lowest evaporating temperature of water is 0 °C. This pair follows flat isothermal adsorption cooling technology because of the greater latent heat of $H_2O$ compared to methanol or other conventional refrigerants. It also has a significant adsorption heat of approximately 300–4200 kJ/kg, which is greater than that of the silica gel–water pair [4].

Temperatures greater than 70° C arise in the system during the desorption process. Moreover, this pair remains stable within a very high temperature range. As a result, this pair is suitable for recovering latent heat at temperatures greater than 200 °C. It also shows a similar performance within different condensation temperatures because the sorption isotherm is independent from the variation of condensation pressure [70]. However, the drawback of this pair is that it is not applicable for evaporation at temperatures below 0 °C. Therefore, the mass transfer performance is lower if the working pressure is low. Moreover, it requires a longer cycle time due to the high temperature of the sorption process [77].

Different studies and various experiments have been performed to determine the best performance of zeolite-water working pairs. For example, Poyelle et al. [78] described two different SCPs (specific cooling power per kilogram of adsorbent) for a zeolite–water pair at different temperatures. At 4 °C (during evaporation), the SCP was 97 W/kg, while the SCP increased to 135 W/kg at higher evaporation temperatures. They also suggested that the SCP can be increased (to approximately 600 W/kg) by improving the mass transfer performance through the use of a certain material [4]. Zhang [79] designed an automobile refrigeration system where a zeolite13X-water pair was used. Considering different thickness, Tatlier et al.[80] also studied the COP of zeolite13X-water working pair. A reversible two-bed zeolite/water pump with a simulated model was offered by Cacciola et al. [81]. A prediction was made by Jones [82] that the COP can be increased to 2.5 if a six-bed zeolite/water system is used. Zhu et al.[83] implemented a medium-size adsorption cooling system with a zeolite13X-water pair for producing chilled water. This system was operated with the wasted heat from an engine and was used to preserve liquid products in fishing boats [4].

*3.2.1.3. Activated carbon granular and fiber adsorbent.* Activated carbon is formed at a very high temperatures (700–1100 °C); the material with carbon is thermally decomposed and then made active with $CO_2$ or steam [84]. The large surface area, higher adsorption capacity, higher surface reactivity and suitable pore size are advantageous characteristics of this pair that lead to its use in physisorption cooling systems. For example, Bansal and Goyal [85] found that there was approximately 800–1500 $m^2$/g of surface area for most used forms of activated-carbon. They showed that the micropores (diameter $<$ 2 nm) are more efficient than mesopores (diameter>50 nm) in an adsorption process. This pair has a lower heat of adsorption compared to other physical adsorbent pairs [72]. Though there is a high thermal resistance between the contact of the adsorber wall and the fiber, the carbon fiber is preferable for its larger surface area, better performance in heat and mass transfer and uniformly distributed pores compared to the granular carbon [86].

Both the fiber and the granular activated carbon allow for ammonia, methanol and ethanol to be used as refrigerants for their suitable features in a cooling system. For example, methanol with active-carbon is more preferable for having a low desorption-temperature (100 °C) and adsorption heat (1800–2000 kJ/kg). Moreover, this pair has a larger cycle capacity and latent heat evaporation, indicating the largest COP in activated-carbon physisorption systems [87]. For example, Saha et al. [88] studied an activated-carbon fiber ethanol chiller and concluded that the adsorption capacity could be increased 2–3 times with this pair if the COP was increased by 10–20%. However, methanol requires a larger vacuum space, is chemically toxic and has poor thermal conductivity from having a decomposition temperature of more than 120 °C [89]. Passos et al. [90] conducted a comparative study on the performance of methanol with three different activated-carbons for an adsorption cooling system. An experiment was performed by Rudenko et al. [91] using alkyl-amine, ammonia, methanol and ethanol with activated-carbon. They found that in spite of having almost the same saturation pressure of ethanol and methanol, methanol had approximately 30% more latent heat during the vaporization than ethanol, which implied a higher cooling capacity. They concluded that though methanol has a higher adsorption capacity compared to ammonia, it also had problems with leakage and toxicity issues.

*3.2.1.4. Activated carbon–methanol adsorbent.* A higher adsorption capacity, lower adsorption heat (approximately 1800–2000 kJ/kg)

and desorption temperature and larger evaporation latent heat are the primary features of the activated-carbon/methanol pair [89, 92]. It has the largest COP when methanol is used with the activated-carbon pair [87]. This pair is suitable for solar energy because of its lower desorption temperature (approximately 100 °C). However, Hu [89] suggests that this pair should not be used at temperatures above 120 °C to avoid decomposition of the methanol. He also showed that when the temperature exceeds 150 °C, dimethyl-ether is produced from the decomposition of their activated-carbon and methanol. Methanol also has higher toxicity, requires more vacuum space and reduces system performance with non-condensable gases. Moreover, activated-carbon has lower thermal conductivity, acting as an insulator, which causes a decrease in the COP of the entire system [93].

*3.2.1.5. Activated carbon–ammonia adsorbent.* Though the activated-carbon/ammonia pair has the same adsorption heat, it is more preferable than the activated-carbon/methanol pair because it has a larger working pressure (approximately 16 bar) and allows better performance in heat and mass transfer as well as reducing the cycle-time within the condensation process at a temperature of 40 °C. It is also more suitable than the activated-carbon/methanol pair for heat sources of 200 °C or higher [94, 95].

The SCP of the system can be increased by resisting the leakage of air. In fact, the higher cooling capacity, the increased heat and mass transfer, the accessibility of heat sources and the greater working temperature range are features of this pair that have attracted significant research. [96, 97]. Tamainot-Telto and Critoph [96] designed a two-bed system with a monolithic-carbon/ammonia pair where they found the adsorbent rate of 600 W/kg at a desorption temperature of 100 °C. Wang et al. [94] investigated the performance of an activated-carbon/ammonia pair and found that ammonia has a 33% lower adsorption quantity (0.29 kg/kg) compared to methanol (0.45 kg/kg). Though the leakage problem has been overcome by improved technology, there are still other problems such as the corrosiveness, bad smell and toxicity of ammonia, all of which impede the expanded use of this pair [96]. A summarization of above-mentioned physisorption systems is provided in Table 2.

### 3.2.2. Solar chemisorption cooling systems

Chemisorption is a process in which the adsorbate and the adsorbent atoms form a complex compound by sharing their electrons in a chemical reaction process. A valence force is created that is stronger than the van der Waals interaction described in the physisorption process. To free the adsorbate, a very high heat of up to 800 kJ/mole is required. It is a specific process that is suitable for a fixed gas and a fixed solid adsorbent. Moreover, it is a monovariant system, where physisorption is a divariant technique [2].

A high COP is the primary advantage of chemisorption technology [101]. For example, a pair of $CaCl_2$ (calcium chloride) and $CO_2$ was used in a reactor that was capable of storing a maximum heat of 900 °C, a decarbonation of $CaCO_3$ (calcium carbonate) and up to 997 °C for generation by calcium oxide (CaO). However, the agglomeration, swelling and disintegration of the adsorbent have a negative impact on the COP of this technology. However, using a porous matrix in the adsorbent can improve the COP [102]. Oliveira et al. [103] suggested that the COP can be significantly improved by increasing the cooling capacity and operating with multiple (double or triple) heating and cooling effects.

The force produced during the chemical reaction includes coordination, oxidation, hydrogenation and complexation. A complete cycle of chemisorption technology consists of four consecutive processes: desorption, condensation, evaporation and adsorption [70]. The typical working pairs for chemisorption are metal chloride–ammonia [104], metal hydride–hydrogen [105] and metal oxides–oxygen [106, 107].

*3.2.2.1. Metal chloride–ammonia adsorbent.* In a chemisorption system, the complexation reaction occurs between the refrigerants and the metal chlorides and forms a coordinated compound. The coordinate bond theory states that when a hybrid orbital is created by a center atom and that orbital is occupied by the lone-electron-pair, a coordinate bond is formed. There are some metals that react with chlorine to form an expected metal–chloride pair, such as calcium, magnesium, barium and strontium, but $CaCl_2$ is widely used in adsorption technology [72].

The calcium chloride-ammonia pair is one of the most well-known pairs for the chemical adsorption system. The cycle adsorption capacity of a $CaCl_2$–$NH_3$ pair is impressive. One mole of $CaCl_2$ can react with eight moles of $NH_3$; consequently, the pair combination of $CaCl_2$–$8NH_3$ that depends on various desorption pressures and temperatures [4]. The reaction between $CaCl_2$ and $NH_3$ can be represented by the following chemical equation:

$$CaCl_2.n_1NH_3 \leftrightarrow CaCl_2.(n_1-n_2)NH_3+n_2NH_3-\Delta H$$

where $\Delta H$ denotes the enthalpy (J/mole) changes in the reaction and $n1$, $n2 \rightarrow 2,4$ and 8 [72].

This pair is more applicable in ice-making because it has a low boiling point. Several simulations and experiments have been performed with this pair for cooling purposes [108,109]. This system requires more space for installation, and the engine radiates more heat to the environment through exhaust gas. Fishing boats are the most suitable place to install this system for ice-making purposes. Wang et al. [110,111] designed and implemented a heat-pipe type $CaCl_2$–$NH_3$ cooling system that was particularly applicable for ice-making in fishing boats. They calculated a SCP of approximately 731 W/kg and a COP of 0.38.

Tokarev et al. [112] conducted an experiment of $CaCl_2$ with the MCM-41 host matrix that showed an enormous capacity for water adsorption and energy storage. MCM-41 contained some mesopores that resembled monosized cylinders that were capable of absorbing up to 0.75 g of water per gram of dry sorbent. Dellero and Touzain [113] analyzed five different carbon-fiber compounds to run a chemical heat pump. They concluded that a faster agglomeration system can be achieved by using two compounds, named GFIC and IFC. Another simulation was performed by Iloeje et al. [109], which showed that the agglomeration can be controlled by using 20% of $CaSO_4$ with the adsorbent.

The higher adsorption quantity (1 kg/kg for most of the chlorides) is the primary advantage of metal-chloride/ammonia pairs, but it is not free from the agglomeration and salt swelling that resists mass and heat transfer. Moreover, there are some obstacles to using the $CaCl_2$–$NH_3$ pair, such as corrosion, decomposition, expansion and deterioration [93].

*3.2.2.2. Metal hydrides and hydrogen.* There are four different types of hydrides of hydrogen because it is capable of forming chemical compounds with almost every element. With the metals of groups IA and IIA, hydrogen can create salt hydrides such as NaH and $CaH_2$ because it is highly reactive with other elements with a low electronegativity. The metal hydrides form with the reaction of transition metals, in which the parental metal attracts the hydrogen atom into its crystal lattice. There are two special types of hydrides: non-metal molecular hydrides and covalent high-polymerized hydrides. An acceptable performance in an adsorption cooling system can be achieved by using the metal hydrides and the salt hydrides pairs. The salt hydrides are more

**Table 2**
The properties of working pairs observed in different physisorption refrigeration systems.

| Working fluids (Pairs) | Solutions | | Features/results | Sources |
|---|---|---|---|---|
| | Refrigerants | Absorbents | | |
| Silica gel | Water | Silica-gel | • The pair shows better performance up to 200 °C; hence, the COP decreases for overheating problems<br>• Water shows better performance, as it has more latent heat than others, allows for running within very low temperatures | [70]<br>[74,75] |
| Zeolite–water | Water | Zeolite | • Because the water has an evaporation temperature of 0 °C; this pair is widely applicable for air conditioning purposes<br>• It shows the better stability up to a temperature of 200 °C<br>• By using specific materials, the SCP can be made higher (600 W/kg) | [4]<br>[70]<br>[78] |
| Activated carbon granular and fiber | Ammonia, methanol, ethanol | Activated carbon granular and fiber | • The carbon fiber is more preferable for its larger surface area, ensuring better performance in heat and mass transfer<br>• Methanol is the widely used refrigerant with this pair because it has a low desorption temperature (100 °C) and large evaporation latent heat<br>• The activated carbon fiber with ethanol chiller shows 10–12% more COP with 2–3 times increment of adsorption capacity | [86,98]<br>[87]<br>[88] |
| Activated carbon–methanol | Methanol | Activated carbon | • The pair exhibits the largest COP with methanol as the refrigerant<br>• To avoid the decomposition of methanol, the pairs should be used with temperatures below 120 °C<br>• It has lower thermal conductivity as an insulator | [87,99]<br>[89]<br>[93] |
| Activated carbon–ammonia | Ammonia | Activated carbon | • The pair has higher cooling capacity, accessibility of larger working temperature and better heat and mass transfer<br>• Ammonia has 33% lower adsorption quantity (0.29 kg/kg) than methanol (0.45 kg/kg); the pair may struggle with problems of corrosion, leakage and toxicity | [96,97,100]<br>[96] |

suitable because of their hexagonal crystal-lattice, which has a higher density compared to the simple metals. During this process, the hydrogen atom acts as a proton and enters into the hexagonal crystal-lattice, much like a metallic bond [72].

Temperature and pressure are the main factors affecting the performance in an adsorption system for the metal hydrides–hydrogen pair. Libowitz et al. [114] described metal hydrides and metal matrix alloys that could be used for achieving better system performance. For example, advanced-porous-metal-hydrides (PMHs) are more efficient in heat and mass transfer. Metals such as nickel, Fe (iron), and aluminum are used to make mischmetal (Mm) matrix alloys that have significant reaction heat and greater quantity for the adsorption process. Though this pair has a low SCP, it can be highly utilized in condensers and evaporators. Moreover, this pair provides a solution for limited space problems because it has a high density (6.5–8 kg/L) that helps to increase the volumetric cooling capacity [115]. The working principle of an adsorption cycle for metal-hydrides/hydrogen pair differs from the physisorption or chemisorption process because there are no saturated refrigerants. Most of the pairs follow the hysteresis phenomenon during the adsorption and desorption process. The pressure varies with different ranges within the entire transition process with respect to the hydrogen quantity [114].

*3.2.2.3. Metal oxides and oxygen.* Oxygen can be found in molecular or atomic form. The metal oxides and oxygen pair refers to a system where a metal adsorbs the oxygen atoms. A metal oxide is formed when oxygen is adsorbed inside the lattice of a metal. The adsorption of oxygen (atomic or molecule) depends on the type and external situation of that metal. In addition to this adsorption, the desorption of oxygen atoms may occur during the process of desorption and the heating of that system. Moreover, some oxygen molecules become stable and remain inside the metal; some form of activated energy is required to induce this transition [4].

The metal oxides help to perform the oxidation and deoxidation process. Kato et al. [116] designed a heat pump in which oxygen was used as a refrigerant and metal oxides were used as adsorbents. They used calcium oxide and magnesium oxide in different experiments with high temperature gas reactors. The results of the experiments indicated that 1 MW of energy could be produced within one hour by taking a quantity of CaO of approximately 2.85 $m^3$ with a temperature and pressure of 998 °C and 4 atm, respectively. Haruta [117] used gold nanoparticles(below 10 nm) with a base metal oxide and showed that the system performance could be increased by keeping the temperature low. He concluded that the performance of the catalysts was dependent on the size of the particles, the support selection and the contact structure, with the last factor playing the most important role for reaction. However, this pair is not free from agglomeration and swelling problems.

### 3.2.3. Hybrid adsorption pairs

In the above discussion, we observed that in chemisorption technology, a single pair is not able to fulfill all of the requirements for providing the best cooling. Therefore, some suggestions are offered to use more than one pair of working fluids as composite adsorbents [118]. Hybrid adsorption has focused on two main objectives:

1. To develop the performance in transferring the heat as well as the mass. Heat transfer is resisted by salt swelling, and mass transfer is reduced for salt agglomeration. Therefore, the hybrid adsorbents can avoid these problems with high thermal conductivity and a porous structure [119].
2. By adding chemical adsorbents to physical adsorbents, the adsorption capacity of the system is increased [120].

The most common working pairs used in hybrid adsorption technology are silica gel–chlorides–water [121,122] and ammonia-chlorides-porous media [123].

**Table 3**
Features of the working fluids used in chemisorption cooling systems.

| Cooling systems | Working fluids (pairs) | Features/results | Sources |
|---|---|---|---|
| Chemisorption cooling system (single pairs) | Metal-chloride/ ammonia | • Lower boiling point, can be used for ice making, SCP=731 W/kg, COP=0.38.<br>• A solution of 20% $CaSO_4$ can reduce the agglomeration problem by mixing it with the working fluids<br>• Corrosion, decomposition, expansion and deterioration are the main problems | [110,111]<br>[109]<br>[93] |
| | Metal- hydrides/ hydrogen | • Can be widely used in condenser and evaporator because it has higher density (6.5–8 kg/L) and requires small spaces<br>• There is no saturated refrigerant; hence the cycle follows the hysteresis phenomenon | [115]<br>[114] |
| | Metal oxides/oxygen | • 1 MW energy can be achieved by using 2.85 $m^3$ of CaO within 1st hour at a temperature of 998 °C<br>• The nanoparticles (10 nm) can be used to increase the system performance | [116,130,131]<br>[117] |
| Hybrid chemisorption cooling systems (composite pairs) | Silica gel/chloride/ water | • Adsorption capacity is increased six times compared to standalone chloride/ water pair<br>• Small pore of silica gel increases the adsorption performance and the rate of heat and mass transfer<br>• The $CaCl_2$ of larger concentration shows the higher adsorption capacity | [112,124,132]<br>[124]<br>[125] |
| | Chlorides/porous media/ammonia | • The dimensional stability can be achieved by using the pairs with a density of 156 kg/$m^3$<br>• When the number of cycles increases, the COP decreases because $MnCl_2$ separates from the fibers | [127,133]<br>[113,134] |

*3.2.3.1. Silica gel and chloride/water.* Silica-gel plays the most important role in increasing adsorption quantity. By using silica-gel with chloride-water (e.g., $CaCl_2$-$H_2O$), the adsorption capacity increases approximately six-fold compared to the adsorption process without silica-gel. This hybrid pair is produced through an impregnation process [112,124]. The process combines a salty solution with the silica-gel, which is then dried.

Aristov et al. [124] introduced some changes in the pore structures of silica-gel and used different types and quantities of salt to overcome the issues of agglomeration and salt swelling. They concluded that a smaller pore of silica-gel increased the adsorption performance and a better proportion of silica-gel and salt was also responsible for increasing the heat and mass transfer. Daou [125] performed a comparative study of the silica gel–$CaCl_2$–$H_2O$ pair with various concentrations of $CaCl_2$. He examined a range of zero to 50% of $CaCl_2$ solution and concluded that the adsorption capacity was higher when using a higher concentrated $CaCl_2$, as the salt was easily liquefied within the compound at a higher concentrated solution.

*3.2.3.2. Chlorides, porous media and ammonia.* The chlorides/porous media/ammonia pair is formed with four different categories of porous-media: expanded-graphite, activated-carbon, activated-carbon-fiber and vermiculite. To increase the rate of heat transfer as well as the mass transfer, the first option is more suitable than others because it works without any expansion in the entire adsorption process. The graphite should be expanded before mixing with chlorides. To extract the humidity, the graphite powder must be kept at a low temperature for a few hours. The graphite expands within a temperature range of 300–700 °C for a few minutes or hours. This expansion significantly changes the structure, which can be observed with a SEM (scanning electron microscope) [126].

Mauran et al. [127] conducted a study on a pair of expanded graphite-$CaCl_2$. In terms of dimensional stability, they concluded that with a density of 156 kg/$m^3$ in the graphite block, the rate of volume expansion was null. Another study on the same pair showed the high performance of hybrid pairs and mentioned that a SCP of approximately 1000 W/kg $CaCl_2$ could be achieved if the mass ratio of the adsorbents was 1:1 with a temperature range of −20 °C to −10 °C for evaporation [123,124].

On the other hand, the activated carbon/$CaCl_2$ pair is suitable for overcoming the salt agglomeration problem, which can improve the heat and mass transfer performance. Therefore, some hybrid adsorbents do have agglomeration and swelling issues. Wang et al.[128] developed a system that considered the swelling space for ice-making on fishing-boats. They used a ratio of 2:1 for swelling space, $CaCl_2$ and pure $CaCl_2$, and 1:1 for the hybrid adsorbent with an addition of activated-carbon. The results from the investigation of this system showed that these hybrid pairs had 40% more refrigeration density than other typical single-pair adsorbents.

The chlorides with activated carbon fiber are capable of improving the capacity of heat transfer. There are two types of carbon fibers used for hybrid adsorption technology, ICFs (impregnated carbon fibers) with $MnCl_2$ and GFICs (graphite fibers intercalation compounds). The activated-carbon fibers are mixed with an alcoholic solution of manganese chloride; once the solvent is eliminated, the ICFs remain. However, the drawback of this pair is that the increased cycles of operation can cause the $MnCl_2$ to separate from the fibers, reducing the COP of the entire chemisorption process [113]. Instead of using alcohol, water was used as a solvent in the pair of activated-carbon fibers with salt in an experiment performed by Vasiliev et al. [129]. A 2–3 mm thin film cover of salt was found over the surface of the carbon-fiber, which was more applicable for $NH_3$ as a refrigerant. A summary of these chemisorption cooling systems is presented in Table 3.

## 4. Conclusions

In summary, more countries are endeavoring to exploit renewable energy than ever before. Pollution, higher expenses and limited resources are the main obstacles to the widespread use of fossil fuels. Therefore, renewable energy sources, such as solar energy, have been of considerable interest because of their promising advantages.

Because of the year-round availability of sunshine, solar energy can be easily captured all over the world. Though the solar photovoltaic system can provide electricity as well as refrigeration, solar thermal refrigeration is much more efficient. Solar thermal cooling technologies are being used all over the world for industrial and home cooling purposes. These cooling systems are more applicable in remote areas or islands where conventional cooling is difficult and solar energy is always available. These systems are also more suitable than conventional refrigeration systems because pollution-free working fluids (instead of chlorofluorocarbons) are used as refrigerants.

This study also summarizes the different working fluids of solar absorption cooling systems and adsorption cooling systems, providing various results with their advantages and limitations. Though the coefficient of performance of absorption cooling systems is better than that of adsorption systems, the higher temperature issues can be easily handled with solar adsorption systems. Moreover, solar hybrid cooling systems can provide higher capacity and better coefficients of performance by eliminating some of the problems encountered with individual working pairs.

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